

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

215505US0XPCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/926479

INTERNATIONAL APPLICATION NO.
PCT/EP00/02799INTERNATIONAL FILING DATE
30 March 2000PRIORITY DATE CLAIMED
12 May 1999

TITLE OF INVENTION

ANTIMICROBIAL COPOLYMERS

APPLICANT(S) FOR DO/EO/US

OTTERSBACH Peter Zum Beuel et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
- ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
- ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
- ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report/Request for Priority
PCT/IB/308

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/926479

INTERNATIONAL APPLICATION NO.

PCT/EP00/02799

ATTORNEY'S DOCKET NUMBER

215505US0XPCT

24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- ☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00
- ☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00
- ☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00
- ☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).

☐ 20 ☒ 30

\$130.00

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	- 20 =	0	x \$18.00
Independent claims	- 3 =	0	x \$84.00

Multiple Dependent Claims (check if applicable).

☐

\$0.00

TOTAL OF ABOVE CALCULATIONS =

\$1,020.00

Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.

\$0.00

SUBTOTAL =

\$1,020.00

Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).

☐ 20 ☐ 30

+

\$0.00

TOTAL NATIONAL FEE =

\$1,020.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

☐

\$0.00

TOTAL FEES ENCLOSED =

\$1,020.00

Amount to be:

refunded

\$

charged

\$

- a. ☒ A check in the amount of \$1,020.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



22850

Surinder Sachar
Registration No. 34,423

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE

Nov. 9 2001

FORM PTO-1390 (Modified)
(REV 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

215505US0XPCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/926,479

INTERNATIONAL APPLICATION NO.
PCT/EP00/02799INTERNATIONAL FILING DATE
30 March 2000PRIORITY DATE CLAIMED
12 May 1999

TITLE OF INVENTION

ANTIMICROBIAL COPOLYMERS

APPLICANT(S) FOR DO/EO/US

Peter OTTERSBAACH et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☐ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☒ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☐ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☒ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notification of Missing Requirements

Response to Notification of Missing Requirements

Amended Sheets (Pages 2, 3, 4, 6, 7, 8, 9, 14, 15, 16, 17, 18, 19, 20, 21, and 22)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/926,479	INTERNATIONAL APPLICATION NO. PCT/EP00/02799	ATTORNEY'S DOCKET NUMBER 215505US0XPCT
---	--	--

24. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

- | | |
|--|------------------|
| <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO | \$1040.00 |
| <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO | \$890.00 |
| <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO | \$740.00 |
| <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) | \$710.00 |
| <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) | \$100.00 |

ENTER APPROPRIATE BASIC FEE AMOUNT =

CALCULATIONS PTO USE ONLY

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
---------------	---------------------	---------------------	-------------	--

Total claims	22 - 20 =	2	x \$18.00	\$36.00
--------------	-----------	---	-----------	----------------

Independent claims	2 - 3 =	0	x \$84.00	\$0.00
--------------------	---------	---	-----------	---------------

Multiple Dependent Claims (check if applicable).	<input type="checkbox"/>	\$0.00
--	--------------------------	---------------

TOTAL OF ABOVE CALCULATIONS =

Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.	<input type="checkbox"/>	\$0.00
--	--------------------------	---------------

SUBTOTAL =

Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).	<input type="checkbox"/>	\$0.00
--	--------------------------	---------------

TOTAL NATIONAL FEE =

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).	<input type="checkbox"/>	\$0.00
---	--------------------------	---------------

TOTAL FEES ENCLOSED =

01/29/2002 1:30 PM RECEIVED 0926479		
-------------------------------------	--	--

01 FEB 02 09:00 AM		
--------------------	--	--

Amount to be:	\$
refunded	
charged	\$

- a. ☐ A check in the amount of **\$36.00** to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☐ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Surinder Sachar
Registration No. 34,423



22850

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE

Jan 25 2002

215505US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
PETER OTTERSBAACH ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: 09/926,479 :
FILED: NOVEMBER 9, 2001 :
FOR: ANTIMICROBIAL COPOLYMERS:

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please cancel Claims 19-22.

Please amend the claims as shown in the marked-up copy following this amendment to read as follows.

1. (Amended) An antimicrobial copolymer obtained by copolymerizing (component I) one or more aliphatically unsaturated monomers, said one or more aliphatically unsaturated monomers functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group, with (component II) one or more second aliphatically unsaturated monomers, said one or more second aliphatically unsaturated monomers at least

09/926,479 "015505"

singly functionalized by means of an amino group, wherein component I and component II are different.

2. (Amended) The antimicrobial copolymer as claimed in claim 1, wherein component II comprises one or more second aliphatically unsaturated monomers, said one or more second aliphatically unsaturated monomers at least singly functionalized by means of a tertiary amino group.

3. (Amended) The antimicrobial copolymer as claimed in claim 1, wherein component I comprises one or more aliphatically unsaturated monomers, said one or more aliphatically unsaturated monomers comprising an ester group at least singly functionalized by means of an amino group.

4. The antimicrobial copolymer as claimed in Claim 1, wherein component I comprises one or more acrylates or one or more methacrylates, said one or more acrylates or said one or more methacrylates at least singly functionalized by means of a tertiary amino group.

5. (Amended) The antimicrobial polymer as claimed in claim 1, wherein each of components I and II is an aliphatically unsaturated monomer functionalized by means of a tertiary amino group, said tertiary amino group having the formula



where R^1 : is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R^2 and R^3 : are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have

substitution by O atoms, N atoms or S atoms, where R^2 and R^3 are identical or different,

wherein R^1 comprises at least one ester group.

6. (Amended) An antimicrobial coating comprising the antimicrobial copolymer as claimed in claim 1, wherein component I and component II are copolymerized on a substrate.

7. (Amended) An antimicrobial coating comprising the antimicrobial copolymer as claimed in claim 1, wherein component I and component II are graft polymerized on a substrate.

8. (Amended) The antimicrobial coating as claimed in claim 7, wherein the substrate is activated prior to graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ -radiation.

10. (Amended) A process for preparing an antimicrobial copolymer comprising copolymerizing (component I) one or more aliphatically unsaturated monomers, said one or more aliphatically unsaturated functionalized by means of an ester group and a tertiary amino group, with (component II) one or more second aliphatically unsaturated monomers, said one or more second aliphatically unsaturated monomers at least singly functionalized by means of an amino group, wherein components I and II are different.

11. (Amended) The process as claimed in claim 10, wherein component II comprises one or more second aliphatically unsaturated monomers, said one or more second aliphatically unsaturated monomers at least singly functionalized by means of a tertiary amino group.

12. (Amended) The process as claimed in claim 10, wherein component I comprises one or more aliphatically unsaturated monomers, said one or more aliphatically unsaturated

monomers comprising an ester group at least singly functionalized by means of an amino group.

13. (Amended) The process as claimed in claim 10, wherein component I comprises one or more acrylates or one or more methacrylates, said one or more acrylates or one or more methacrylates at least singly functionalized by means of a tertiary amino group.

14. (Amended) The process as claimed in claim 10, wherein each of components I and II is an aliphatically unsaturated monomer functionalized by means of a tertiary amino group, said tertiary amino group having the formula



where R^1 : is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R^2 and R^3 : are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms, where R^2 and R^3 are identical or different,

wherein R^1 comprises at least one ester group.

15. (Amended) The process as claimed in claim 10, wherein component I and component II are copolymerized on a substrate.

16. (Amended) The process as claimed in claim 10, wherein component I and component II are graft polymerized on a substrate.

17. (Amended) The process as claimed in claim 16, wherein the substrate is activated prior to graft polymerization by UV radiation, plasma treatment, Corona treatment, flame treatment, ozonization, electrical discharge or γ -radiation.

Please add the following new claims.

23. (New) An article of manufacture comprising an antimicrobial coating, said antimicrobial coating comprising the antimicrobial copolymer claimed in Claim 1.
24. (New) A medical device comprising an antimicrobial coating, said antimicrobial coating comprising the antimicrobial copolymer claimed in Claim 1.
25. (New) A hygiene item comprising an antimicrobial coating, said antimicrobial coating comprising the antimicrobial copolymer claimed in Claim 1.
26. (New) A surface coating, protective paint or other coating comprising the antimicrobial copolymer claimed in Claim 1.

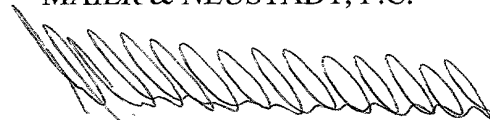
09926479 04306

REMARKS

Claims 1-18 and 23-26 are active in the present application. Claims 19-22 have been cancelled. Claims 23-26 are new claims. Support for the new claims is found in the original claims. Claims 1-8, 10-17 have been amended to remove multiple dependencies and for clarity. No new matter is believed to have been added. An action on the merits and allowance of the claims is solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
Attorney of Record
Registration No. 24,618

Stefan U. Koschmeider, Ph.D.
Registration No. 50,238



22850

(703) 413-3000
Fax #: (703) 413-2220
SUK/law
I:\atty\SUKOS\215505US-pr.wpd

09926479 012502

Marked-Up Copy

Serial No:

1-25-2002

Amendment Filed on:

IN THE CLAIMS

Please cancel Claims 19-22.

Please amend the claims as shown in the marked-up copy following this amendment to read as follows.

1. (Amended) An antimicrobial copolymer [obtainable] obtained by copolymerizing (component I) one or more aliphatically unsaturated monomers, [which have been] said one or more aliphatically unsaturated monomers functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group, with (component II) [another] one or more second aliphatically unsaturated monomers, [monomer which has been] said one or more second aliphatically unsaturated monomers at least singly functionalized by means of an amino group, [where] wherein component I and component II are different [from one another].

2. (Amended) The antimicrobial copolymer as claimed in claim 1, wherein component II [is composed of] comprises one or more second aliphatically unsaturated monomers, [which have been] said one or more second aliphatically unsaturated monomers at least singly functionalized by means of a tertiary amino group.

3. (Amended) The antimicrobial copolymer as claimed in claim 1 [or 2], wherein component I [is composed of] comprises one or more aliphatically unsaturated monomers,

[whose] said one or more aliphatically unsaturated monomers comprising an ester group [has been] at least singly functionalized by means of an amino group.

4. The antimicrobial copolymer as claimed in [one of claims 1 to 3] claim 1, wherein component I [is composed of acrylate or] comprises one or more acrylates or one or more methacrylates, [which have been] said one or more acrylates or said one or more methacrylates at least singly functionalized by means of a tertiary amino group.

5. (Amended) The antimicrobial polymer as claimed in [one of claims 1 to 4] claim 1, wherein each of components I and II is an aliphatically unsaturated monomer functionalized by means of a tertiary amino group, said tertiary amino group [and] having the [general] formula



where R^1 : is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R^2 and R^3 : are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms, where R^2 and R^3 are identical or different,

[with the proviso that R^1 in monomers of component I contains an] wherein R^1 comprises at least one ester group.

6. (Amended) [The antimicrobial coating made from antimicrobial copolymers] An antimicrobial coating comprising the antimicrobial copolymer as claimed in claim 1 [one of claims 1 to 5], wherein

[the copolymerization is carried out on a substrate] component I and component II are copolymerized on a substrate.

7. (Amended) [The antimicrobial coating made from antimicrobial copolymers] An antimicrobial coating comprising the antimicrobial copolymer as claimed in claim 1 [one of claims 1 to 5], wherein [the copolymerization is carried out as a graft polymerization of a substrate] component I and component II are graft polymerized on a substrate.

8. (Amended) The antimicrobial coating as claimed in claim 7, wherein the substrate is activated prior to [the] graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ -radiation.

10. (Amended) A process for preparing an antimicrobial copolymer comprising [copolymers by] copolymerizing (component I) one or more aliphatically unsaturated monomers [which have been] , said one or more aliphatically unsaturated functionalized by means of an ester group and a tertiary amino group, with (component II) [another] one or more second aliphatically unsaturated monomers, said one or more second aliphatically unsaturated monomers [monomers which has been] at least singly functionalized by means of an amino group, [where] wherein components I and II are different [from one another].

11. (Amended) The process as claimed in claim 10, wherein component II [is composed of] comprises one or more second aliphatically unsaturated monomers, [which have been] said one or more second aliphatically unsaturated monomers at least singly functionalized by means of a tertiary amino group.

12. (Amended) The process as claimed in claim 10 [or 11], wherein component I [is composed of] comprises one or more aliphatically unsaturated monomers, [whose] said one or more aliphatically unsaturated monomers comprising an ester group [has been] at least singly functionalized by means of an amino group.

13. (Amended) The process as claimed in [one of claims 10 to 12] claim 10, wherein component I [is composed of acrylate or] comprises one or more acrylates or one or more methacrylates, [which have been] said one or more acrylates or said one or more methacrylates at least singly functionalized by means of a tertiary amino group.

14. (Amended) The process as claimed in [one of claims 10 to 13] claim 10, wherein each of components I and II is an aliphatically unsaturated monomer functionalized by means of a tertiary amino group, [and] said tertiary amino group having the [general] formula



where R¹: is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R² and R³: are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms, where R² and R³ are identical or different,

[with the proviso that R¹ in monomers of component I contains an ester group] wherein R¹ comprises at least one ester group.

15. (Amended) The process as claimed in [one of claims 10 to 14] claim 10, wherein [the copolymerization is carried out on a substrate] component I and component II are copolymerized on a substrate.

16. (Amended) The process as claimed in [one of claims 10 to 15] claim 10, wherein [the copolymerization is carried out as a graft polymerization of a substrate] component I and component II are graft polymerized on a substrate.

17. (Amended) The process as claimed in claim 16, wherein the substrate is activated prior to [the] graft polymerization by UV radiation, plasma treatment, Corona treatment, flame treatment, ozonization, electrical discharge or γ -radiation.

Claims 23-26 (New).

0906479 1012503

CREAVIS Gesellschaft für Innovation
und Technologie mbH
PATENTE ♦ MARKEN

Antimicrobial copolymers

The invention relates to antimicrobial polymers obtainable by copolymerizing aliphatically unsaturated monomers with amino and ester functions with one
5 or more aliphatically unsaturated amino-functionalized monomers, and to a process for preparing the copolymers, and to their use.

The invention further relates to antimicrobial polymers obtainable by graft-
10 copolymerizing ester- and amino-functionalized aliphatically unsaturated monomers, and to a process for preparing the graft polymers, and to their use.

It is highly undesirable for bacteria to become established or to spread on the surfaces of pipelines, containers or packaging. Frequently, slime layers form
15 and permit sharp rises in microbial populations, and these can lead to persistent impairment of the quality of water, drinks or foods, and even to spoilage of the product and harm to the health of consumers.

Bacteria must be kept away from all fields of life in which hygiene is
20 important. This affects textiles for direct body contact, especially in the genital area, and for the care of the elderly and sick. Bacteria must also be kept away from surfaces of furniture and instruments in wards, especially in areas for intensive care and neonatal care, in hospitals, especially in areas for medical interventions, and in isolation wards for critical cases of infection, and also in
25 toilets.

A current method of treating equipment, or the surfaces of furniture or textiles, to resist bacteria, either when this becomes necessary or else as a precautionary measure, is to use chemicals or solutions or mixtures of these which as disinfectants have fairly broad and general antimicrobial action.
30 Chemical agents of this type act nonspecifically and are frequently themselves toxic or irritant, or form degradation products which are hazardous to health. In addition, people frequently exhibit intolerance to these materials once they have become sensitized.

Another method to counteract surface spread of bacteria is to incorporate substances with antimicrobial action into a matrix.

Tert-butylaminoethyl methacrylate is a commercially available monomer in methacrylate chemistry and is used in particular as a hydrophilic constituent in copolymerizations. For example, EP 0 290 676 describes the use of various polyacrylates and polymethacrylates as a matrix for immobilizing bactericidal quaternary ammonium compounds.

In another technical sector US-A 4 532 269 discloses a terpolymer of butyl methacrylate, tributyltin methacrylate and tert-butylaminoethyl methacrylate. This polymer is used as an antimicrobial paint for ships: the hydrophilic tert-butylaminoethyl methacrylate promotes gradual erosion of the polymer, thus liberating the highly toxic tributyltin methacrylate as antimicrobial agent.

In these applications the copolymer prepared using aminomethacrylates is merely a matrix or carrier substance for added microbicidal agents which can diffuse or migrate out of the carrier substance. Sooner or later polymers of this type lose their effectiveness once the "minimal inhibitory concentration" (MIC) is no longer achieved on the surface.

European Patent Applications 0 862 858 and 0 862 859 have disclosed that homo- and copolymers of tert-butylaminoethyl methacrylate, a methacrylate having a secondary amino function, have inherent microbicidal properties. To avoid undesirable resistance phenomena in the microbes, particularly bearing in mind the development of resistance by bacteria known from antibiotics research, systems developed in the future will also have to be based on novel compositions with improved effectiveness.

Antimicrobial terpolymers, which contain amino-functionalized monomers, a high content of ethylene, and optionally further monomers, are known from US 5 208 016.

The object of the present invention is therefore to develop novel polymers having antimicrobial action. These, where appropriate in the form of a coating, should prevent the establishment and spread of bacteria on surfaces.

09926479 01250

"Amended page"

Surprisingly, it has now been found that copolymerizing two or more components of aliphatically unsaturated monomers, of which component I has been functionalized by means of ester groups and tertiary amino groups and component II by means of amino groups, or graft-copolymerizing these components on a substrate, gives polymers with a long-lasting microbicidal surface which is not attacked by solvents or by physical stresses and which does not exhibit migration. This makes it unnecessary to use other biocides.

The present invention therefore provides antimicrobial polymers obtained by copolymerizing (component I) aliphatically unsaturated monomers which have been functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group with (component II) another aliphatically unsaturated monomer which has been at least singly functionalized by means of an amino group, where component I and component II are different from one another.

The present invention also provides a process for preparing antimicrobial polymers obtained by graft-copolymerizing (component I) aliphatically unsaturated monomers which have been functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group with (component II) another aliphatically unsaturated monomer which has been at least singly functionalized by means of an amino group, where components I and II are different from one another.

The copolymers of the invention are prepared by copolymerizing exclusively components I and II. There is no requirement for the use of other aliphatically unsaturated monomers.

Component I may be composed of aliphatically unsaturated monomers whose ester group has been at least singly amino-functionalized, preferably by means of a tertiary amino group. Particularly preferred monomers for component I are acrylates or methacrylates which have been at least singly functionalized by means of a tertiary amino group. Here, too, the preferred position for the amino group is within the ester function.

"Amended page"

The aliphatically unsaturated monomers of components I or II used according to the invention and at least singly functionalized by means of a tertiary amino group may have a hydrocarbon radical of up to 50 carbon atoms, preferably up to 30 carbon atoms, particularly preferably up to 22 carbon atoms. The substituents of the amino group may have aliphatic or vinylic hydrocarbon radicals, such as methyl, ethyl, propyl or acrylic radicals, or cyclic hydrocarbon radicals, such as substituted or unsubstituted phenyl or cyclohexyl radicals having up to 25 carbon atoms. The amino group may also have substitution by keto or aldehyde groups, such as acryloyl or oxo groups. The monomers of component I always contain an ester group.

To achieve a sufficient rate of polymerization, the monomers of components I or II used according to the invention should have a molar mass of less than 900, preferably less than 550 g/mol.

In a particular embodiment of the present invention the components I or II used may comprise aliphatic unsaturated monomers functionalized by means of a tertiary amino group and having the general formula



where R^1 : is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R^2 and R^3 : are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms, where R^2 and R^3 are identical or different,

with the proviso that R^1 in monomers of component I contains an ester group.

The monomers of components I and II must be different. Examples of combinations of monomers of components I and II are given in the examples.

Examples of suitable comonomer building blocks for component I are 2-diethylaminoethyl methacrylate, 2-dimethylaminoethyl methacrylate, N-3-dimethylaminopropylmethacrylamide, 2-diethylaminoethyl acrylate, 2-dimethylaminoethyl acrylate, 3-dimethylaminopropyl acrylate and 3-dimethylamino-2,2-dimethylpropyl acrylate.

Monomers suitable for component II are any aliphatically unsaturated monomers which have at least one amino function. This amino function may be primary, secondary, tertiary or quaternary.

10

Examples of aliphatically unsaturated monomers with at least one primary amino function are 1-amino-2-propene, N-6-aminohexyl-2-propeneamide, N-3-aminopropylmethacrylamide hydrochloride, 2-aminoethyl methacrylate hydrochloride and 3-aminopropyl vinyl ether.

15

Suitable comonomer building blocks having at least one secondary amino function, besides the secondary-amino-functionalized acrylates and methacrylates described in European Applications 0 862 858 and 0 862 859, are ethyl 3-phenylmethylamino-2-butenate, ethyl 3-ethylamino-2-butenate, ethyl 3-methylamino-2-butenate, 3-methylamino-1-phenyl-2-propen-1-one, N-4-methylamino-1-anthraquinoyl(2-methyl)acrylamide, N-9,10-dihydro-4-(4-methylphenylamino)-9,10-dioxo-1-anthraquinyl-2-methylpropenamide, propyl 2-hydroxy-3-(3-triethoxysilylpropylamino)-2-propenoate, 1-(1-methylethylamino)-3-(2-(2-propenyl)phenoxy)-2-propanol hydrochloride, ethyl 3-phenylamino-3-methyl-2-butenate, 1-(1-methylethylamino)-3-(2-(2-propenyloxy)phenoxy)-2-propanol hydrochloride, methyl 2-acrylamido-2-methoxyacetate, methyl 2-acetamidoacrylate, N-tert-butylacrylamide, 2-hydroxy-N-2-propenylbenzamide and N-methyl-2-propenamide.

30 Examples of aliphatically unsaturated monomers having at least one tertiary amino function are 2-diethylaminoethyl methacrylate, 2-dimethylaminoethyl methacrylate, N-3-dimethylaminopropylmethacrylamide, 2-diethylaminoethyl acrylate, 2-dimethylaminoethyl acrylate, 3-dimethylaminopropyl acrylate and 3-dimethylamino-2,2-dimethylpropyl acrylate.

"Amended page"

Other suitable monomeric building blocks are aliphatically unsaturated monomers which have at least one quaternary amino function, e.g. 3-methacryloyl-aminopropyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium chloride, 2-methacryloyloxyethyltrimethylammonium methosulfate, 3-acrylamido-propyltrimethylammonium chloride, trimethylvinylbenzylammonium chloride, 2-acryloyloxyethyl-4-benzoylbenzyltrimethylammonium bromide, 2-acryloyloxyethyltrimethylammonium methosulfate, N,N,N-trimethylammoniummethane bromide, 2-hydroxy-N,N,N-trimethyl-3-[(2-methyl-1-oxo-2-propenyl)oxy]ammoniumpropane chloride, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]ammoniummethane methyl sulfate, N,N-diethyl-N-methyl-2-[(1-oxo-2-propenyl)oxy]ammoniummethane methyl sulfate, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]ammoniummethane chloride, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ammoniummethane chloride, N,N,N-trimethyl-2-[(2-methyl-1-oxo-2-propenyl)oxy]ammoniummethane methyl sulfate and N,N,N-triethyl-2-[(1-oxo-2-propenyl)-amino]ammoniummethane.

The novel antimicrobial copolymers may also be prepared by copolymerizing components I and II on a substrate. This gives a physisorbed coating made of the antimicrobial copolymer on the substrate.

Suitable substrate materials are especially any of the polymeric plastics, such as polyurethanes, polyamides, polyesters and polyethers, polyether block amides, polystyrene, polyvinyl chloride, polycarbonates, polyorganosiloxanes, polyolefins, polysulfones, polyisoprene, polychloroprene, polytetrafluoroethylene (PTFE) or corresponding copolymers or blends, or

"Amended page"

also naturally occurring or synthetic rubbers, with or without radiation-sensitive groups. The novel process may also be used on surfaces of objects made from metal, from glass or from wood and surface-coated or otherwise coated with plastic.

- 5 In another embodiment of the present invention the antimicrobial polymers may be prepared by graft-polymerizing a substrate with the components I and II. The grafting of the substrate allows covalent linking of the antimicrobial polymer to the substrate. Substrates which may be used are any polymeric material, such as the plastics mentioned above.

10

Prior to the graft copolymerization, the surfaces of the substrates may be activated by a variety of methods. Any standard method for activating polymer surfaces may be used here, for example the substrate may be activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ -radiation. The surfaces are usefully freed in advance in a known manner from oils, fats or other contamination, using a solvent.

15

The substrates may be activated using UV radiation in the wavelength range from 170 to 400 nm, preferably from 170 to 250 nm. An example of a suitable radiation source is a Noblelight UV excimer apparatus from HERAEUS, Hanau, Germany. However, mercury vapor lamps are also suitable for substrate activation as long as they emit substantial proportions of radiation in the abovementioned ranges. The exposure time is generally from 0.1 seconds to 20 minutes, preferably from 1 second to 10 minutes.

20

- 25 The activation of the standard polymers with UV radiation may moreover also use a photosensitizer. For this, the photosensitizer, such as benzophenone, is applied to the substrate surface and irradiated. A mercury vapor lamp may again be used here, with exposure times of from 0.1 seconds to 20 minutes, preferably from 1 second to 10 minutes.

"Amended page"

According to the invention, the activation may also be achieved by plasma treatment using an RF or microwave plasma (Hexagon, Technics Plasma, 85551 Kirchheim, Germany) in air, nitrogen or argon atmospheres. The exposures times are generally from 2 seconds to 30 minutes, preferably from 5 seconds to 10 minutes. The energy supplied
5 in the case of laboratory devices is from 100 to 500 W, preferably from 200 to 300 W.

Corona devices (SOFTAL, Hamburg, Germany) may also be used for activation. The exposure times in this case are generally from 1 to 10 minutes, preferably from 1 to 60 seconds.

10 Activation by electrical discharge, electron beam or γ -radiation (e.g. from a cobalt 60 source), and also ozonization, allows short exposure times, generally from 0.1 to 60 seconds.

15 Substrate surfaces may also be activated by flame treatment. Suitable devices, in particular those with a barrier flame front, can readily be constructed or, for example, purchased from ARCOTEC, 71297 Mönsheim, Germany. They may be operated using hydrocarbons or hydrogen as combustion gas. In all cases it is necessary to avoid damage to the substrate by overheating, and this can readily be ensured if the surface
20 of the substrate facing away from the flame treatment side is in intimate contact with a cooled metal surface. Activation by flame treatment is therefore restricted to relatively thin, sheet-like substrates. The exposure times are generally from 0.1 seconds to 1 minute, preferably from 0.5 to 2 seconds. The flames are exclusively nonluminous, and the distances between the substrate surfaces and the outer side of the flame front are
25 from 0.2 to 5 cm, preferably from 0.5 to 2 cm.

The substrate surfaces activated in this way are coated by known methods, such as dipping, spraying or spreading, with components I and II in solution if desired. Solvents which have proven useful are water and water/ethanol mixtures, but other solvents may
30 also be used as long as they are sufficiently capable of dissolving the monomers and give good wetting of the substrate surfaces. Examples of other solvents are

"Amended page"

ethanol, methanol, methyl ethyl ketone, diethyl ether, dioxane, hexane, heptane, benzene, toluene, chloroform, dichloromethane, tetrahydrofuran and acetonitrile. Solutions with monomer contents of from 1 to 10% by weight, for example about 5% by weight, have proven successful in practice and generally give, in a single pass, coherent
5 coatings which cover the substrate surface and have thicknesses which can be more than 0.1 μm .

The graft copolymerization of the monomers (components) applied to the activated surfaces may usefully be initiated by radiation in the short-wave segment of the visible
10 range or in the long-wave segment of the UV range of electromagnetic radiation. For example, the radiation from a UV excimer of wavelengths from 250 to 500 nm, preferably from 290 to 320 nm, is very suitable. Mercury vapor lamps are also suitable here as long as they have substantial proportions of radiation in the abovementioned ranges. The exposure times are generally from 10 seconds to 30 minutes, preferably from 2 to 15
15 minutes.

A graft copolymerization can also be achieved by a process described in European Patent Application 0 872 512 and based on a graft polymerization of monomer molecules and initiator molecules incorporated by swelling.
20

Even with grafting on a substrate surface, the antimicrobial copolymers produced by the novel methods from components I and II show microbicidal or antimicrobial behavior.

If the novel process is used directly on the substrate surface without grafting,
25 conventional free-radical initiators may be added. Examples of initiators which may be used are azonitriles, alkyl peroxides, hydroperoxides, acyl peroxides, peroxoketones, peresters, peroxocarbonates, peroxodisulfate, persulfate and any of the usual photoinitiators, such as acetophenones, α -hydroxyketones, dimethylketals and benzophenone. The polymerization may also be initiated thermally or, as already stated,
30 by electromagnetic radiation, such as UV light or γ -radiation.

Use of the modified polymer substrates

The present invention also provides the use of the novel antimicrobial copolymers to produce antimicrobially active products, and the products per se which are produced in this way. The products may comprise polymer substrates modified according to the invention or consist of these. Products
5 of this type are preferably based on polyamides, polyurethanes, polyether block amides, polyesteramides or -imides, PVC, polyolefins, silicones, polysiloxanes, polymethacrylate or polyterephthalates surface-modified using novel polymers.

Examples of antimicrobially active products of this type are in particular
10 machine parts for food processing, components in air-conditioning systems, roofing, items for bathroom and toilet use, kitchen items, components of sanitary equipment, components of cages or houses for animals, recreational products for children, components of water systems, food packaging, operator units (touch panels) of devices, and contact lenses.

15 The present invention also provides the use, to produce hygiene products or items in medical technology, of the polymer substrates whose surfaces have been modified using novel antimicrobial copolymers. That which has been said above concerning preferred materials applies correspondingly. Examples
20 of hygiene products of this type are toothbrushes, toilet seats, combs and packaging materials. The term hygiene item also includes other objects which may come into contact with a large number of people, such as telephone handsets, stair rails, door handles, window catches, and grab straps and grab handles in public conveyances. Examples of items in medical technology are
25 catheters, tubing, protective or backing films and also surgical instruments.

The novel copolymers or graft polymers may be used anywhere where importance is placed on surfaces with release properties or surfaces which are very free from bacteria, i.e. microbicidal. Examples of application of the
30 novel copolymers are in particular surface coatings, protective paints and other coatings in the following sectors:

Marine: Boat hulls, docks, buoys, drilling platforms, ballast water tanks

Construction: Roofing, basements, walls, facades, greenhouses, sun

protection, garden fencing, wood protection

Sanitary: Public conveniences, bathrooms, shower curtains, toilet items, swimming pool, sauna, jointing, sealing compounds

Requisites for daily life: Machines, kitchen, kitchen items, sponge pads,
5 recreational products for children, food packaging, milk processing, drinking water systems, cosmetics

Machine parts: Air-conditioning systems, ion exchangers, process water, solar-powered units, heat exchangers, bioreactors, membranes

Medical technology: Contact lenses, diapers, membranes, implants

10 Consumer articles: Automobile seats, clothing (socks, sport clothing), hospital equipment, door handles, telephone handsets, public conveyances, animal cages, cash registers, wall-to-wall carpets, wallpapers.

The following examples are given in order to describe the present invention
15 in greater detail, but are not intended to limit its scope as set out in the patent claims.

Example 1:

6 ml of N-3-dimethylaminopropylmethacrylamide (Aldrich), 6 ml of 2-
20 diethylaminoethyl methacrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is
25 stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

30 Example 1a:

0.05 g of the product from Example 1 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus

aureus microbes are now detectable.

Example 1b:

0.05 g of the product from Example 1 is shaken in 20 ml of a test microbial
5 suspension of *Pseudomonas aeruginosa*. After a contact time of 60 minutes,
1 ml of the test microbial suspension is removed, and the number of microbes
in the test mixture is determined. After expiry of this time the number of
microbes has reduced from 10^7 to 10^3 .

10 Example 2:

8 ml of N-3-dimethylaminopropylmethacrylamide (Aldrich), 8 ml of 2-
dimethylaminoethyl methacrylate (Aldrich) and 80 ml of ethanol are charged
to a three-necked flask and heated to 65°C under a stream of argon. 0.2 g of
15 azobisisobutyronitrile dissolved in 6 ml of ethyl methyl ketone is then slowly
added dropwise, with stirring. The mixture is heated to 70°C and stirred at
this temperature for 72 h. After expiry of this time the reaction mixture is
stirred into 0.8 l of n-hexane, whereupon the polymeric product precipitates.
After filtering off the product, the filter cake is washed with 150 ml of n-hexane
to remove any monomer residues still present. The product is then dried in
20 vacuo for 24 hours at 50°C .

Example 2a:

0.05 g of the product from Example 2 is shaken in 20 ml of a test microbial
suspension of *Staphylococcus aureus*. After a contact time of 15 minutes,
25 1 ml of the test microbial suspension is removed, and the number of microbes
in the test mixture is determined. After expiry of this time the number of
microbes has reduced from 10^7 to 10^2 .

Example 2b:

30 0.05 g of the product from Example 2 is shaken in 20 ml of a test microbial
suspension of *Pseudomonas aeruginosa*. After a contact time of 60 minutes,
1 ml of the test microbial suspension is removed, and the number of microbes
in the test mixture is determined. After expiry of this time the number of
microbes has reduced from 10^7 to 10^4 .

Example 3:

5 ml of N-3-dimethylaminopropylmethacrylamide (Aldrich), 7 ml of 3-dimethylaminopropyl ester acrylate (Aldrich) and 60 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

Example 3a:

0.05 g of the product from Example 3 is shaken in 20 ml of a test microbial suspension of Staphylococcus aureus. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time no Staphylococcus aureus microbes are now detectable.

Example 3b:

0.05 g of the product from Example 3 is shaken in 20 ml of a test microbial suspension of Pseudomonas aeruginosa. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^3 .

Example 4:

5 ml of N-3-dimethylaminopropylacrylamide (Aldrich), 8 ml of 2-diethylaminoethyl methacrylate (Aldrich) and 70 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.18 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.6 l of n-hexane, whereupon the polymeric product precipitates.

"Amended page"

After filtering off the product, the filter cake is washed with 140 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

5 Example 4a:

0.05 g of the product from Example 4 is shaken in 20 ml of a test microbial suspension of *Staphylococcus aureus*. After a contact time of 15 minutes, 1 ml of the test suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2 .

10

Example 4b:

0.05 g of the product from Example 4 is shaken in 20 ml of a test microbial suspension of *Pseudomonas aeruginosa*. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^4 .

15

Example 5:

4 g of N-3-dimethylaminopropylmethacrylamide (Aldrich), 5 g of 2-diethylaminoethyl methacrylate (Aldrich), 3 g of methyl methacrylate (Aldrich) and 65 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C.

20

25

Example 5a:

0.05 g of the product from Example 5 is shaken in 20 ml of a test microbial suspension of *Staphylococcus aureus*. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes

30

in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^2 .

Example 5b:

- 5 0.05 g of the product from Example 5 is shaken in 20 ml of a test microbial suspension of *Pseudomonas aeruginosa*. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of microbes has reduced from 10^7 to 10^3 .

10 Example 6:

4 g of N-3-dimethylaminopropylmethacrylamide (Aldrich), 4 g of 2-diethylaminoethyl methacrylate (Aldrich), 2.5 g of butyl methacrylate (Aldrich) and 65 ml of ethanol are charged to a three-necked flask and heated to 65°C under a stream of argon. 0.15 g of azobisisobutyronitrile dissolved in 4 ml of ethyl methyl ketone is then slowly added dropwise, with stirring. The mixture is heated to 70°C and stirred at this temperature for 72 h. After expiry of this time the reaction mixture is stirred into 0.5 l of n-hexane, whereupon the polymeric product precipitates. After filtering off the product, the filter cake is washed with 100 ml of n-hexane to remove any monomer residues still present. The product is then dried in vacuo for 24 hours at 50°C .

20 Example 6a:

0.05 g of the product from Example 6 is shaken in 20 ml of a test microbial suspension of *Staphylococcus aureus*. After a contact time of 15 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined.

- 25 After expiry of this time no *Staphylococcus aureus* microbes are now detectable.

Example 6b:

0.05 g of the product from Example 6 is shaken in 20 ml of a test microbial suspension of *Pseudomonas aeruginosa*. After a contact time of 60 minutes, 1 ml of the test microbial suspension is removed, and the number of microbes in the test mixture is determined. After expiry of this time the number of

"Amended page"

~~microbes has reduced from 10^7 to 10^3 .~~

In addition to the microbicidal action described above with respect to cells of *Pseudomonas aeruginosa* and *Staphylococcus aureus*, all of the samples also exhibited
5 microbicidal action with respect to cells of *Klebsiella pneumoniae*, *Escherichia coli*,
Rhizopus oryzae, *Candida tropicalis* and *Tetrahymena pyriformis*.

05933479 012502

What is claimed is:

1. An antimicrobial copolymer obtainable by copolymerizing (component I) aliphatically unsaturated monomers which have been functionalized by means of an ester group and at least singly functionalized by means of a tertiary amino group with (component II) another aliphatically unsaturated monomer which has been at least singly functionalized by means of an amino group, where component I and component II are different from one another.
2. The antimicrobial copolymer as claimed in claim 1, wherein component II is composed of aliphatically unsaturated monomers which have been at least singly functionalized by means of a tertiary amino group.
3. The antimicrobial copolymer as claimed in claim 1 or 2, wherein component I is composed of aliphatically unsaturated monomers whose ester group has been at least singly functionalized by means of an amino group.
4. The antimicrobial copolymer as claimed in one of claims 1 to 3, wherein component I is composed of acrylate or methacrylates which have been at least singly functionalized by means of a tertiary amino group.
5. The antimicrobial polymer as claimed in one of claims 1 to 4, wherein each of components I and II is an aliphatically unsaturated monomer functionalized by means of a tertiary amino group and having the general formula



where R^1 : is a branched, unbranched or cyclic, saturated or

"Amended page"

unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

R² and R³: are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which may have substitution by O atoms, N atoms or S atoms, where R² and R³ are identical or different,

with the proviso that R¹ in monomers of component I contains an ester group.

6. The antimicrobial coating made from antimicrobial copolymers as claimed in one of claims 1 to 5, wherein the copolymerization is carried out on a substrate.

7. The antimicrobial coating made from antimicrobial copolymers as claimed in one of claims 1 to 5, wherein the copolymerization is carried out as a graft polymerization of a substrate.

8. The antimicrobial coating as claimed in claim 7, wherein the substrate is activated prior to the graft polymerization by UV radiation, plasma treatment, corona treatment, flame treatment, ozonization, electrical discharge or γ -radiation.

9. The antimicrobial coating as claimed in claim 7, wherein the substrate is activated prior to the graft polymerization by UV radiation with a photoinitiator.

10. A process for preparing antimicrobial copolymers by copolymerizing (component I) aliphatically unsaturated monomers which have been functionalized by means

of an ester group and a tertiary amino group with (component II) another aliphatically unsaturated monomer which has been at least singly functionalized by means of an amino group, where components I and II are different from one another.

5
11. The process as claimed in claim 10,
wherein
component II is composed of aliphatically unsaturated monomers which have been at least singly functionalized by means of a tertiary amino group.

10
12. The process as claimed in claim 10 or 11,
wherein
component I is composed of aliphatically unsaturated monomers whose ester group has been at least singly functionalized by means of an amino group.

15
13. The process as claimed in one of claims 10 to 12,
wherein
component I is composed of acrylate or methacrylates which have been at least singly functionalized by means of a tertiary amino group.

20
14. The process as claimed in one of claims 10 to 13,
wherein
each of components I and II is an aliphatically unsaturated monomer functionalized by means of a tertiary amino group and having the general formula



where R¹: is a branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radical having up to 50 carbon atoms which may have substitution by O atoms, N atoms or S atoms, and

30
R² and R³: are branched, unbranched or cyclic, saturated or unsaturated hydrocarbon radicals having up to 25 carbon atoms, which

"Amended page"

may have substitution by O atoms, N atoms or S atoms, where
 R^2 and R^3 are identical or different,
with the proviso that R^1 in monomers of component I contains an ester group.

- 5 15. The process as claimed in one of claims 10 to 14,
wherein
the copolymerization is carried out on a substrate.
- 10 16. The process as claimed in one of claims 10 to 15,
wherein
the copolymerization is carried out as a graft polymerization of a substrate.
- 15 17. The process as claimed in claim 16,
wherein
the substrate is activated prior to the graft polymerization by UV radiation, plasma
treatment, Corona treatment, flame treatment, ozonization, electrical discharge
or γ -radiation.
- 20 18. The process as claimed in claim 17,
wherein
the substrate is activated prior to the graft polymerization by UV radiation with a
photoinitiator.
- 25 19. The use of the antimicrobial copolymers as claimed in one of claims 1 to 9 for
producing products with an antimicrobial coating comprising the copolymer.
- 30 20. The use of the antimicrobial polymers as claimed in one of claims 1 to 9 for
producing items in medical technology with an antimicrobial coating comprising
the copolymer.
21. The use of the antimicrobial copolymers as claimed in one of claims 1 to 9 for
producing hygiene items with an antimicrobial coating comprising the copolymer.

"Amended page"

22. The use of the antimicrobial copolymers as claimed in one of claims 1 to 9 in surface coatings, protective paints or in other coatings.

09936479 01250

0-215448

Declaration and Power of Attorney for Patent Application

Erklärung für Patentanmeldungen mit Vollmacht

German Language Declaration

Als nachstehend benannter Erfinder erkläre ich hiermit an Eides Statt:

daß mein Wohnsitz, meine Postanschrift und meine Staatsangehörigkeit den im nachstehenden nach meinem Namen aufgeführten Angaben entsprechen, daß ich nach bestem Wissen der ursprüngliche, erste und alleinige Erfinder (falls nachstehend nur ein Name angegeben ist) oder ein ursprünglicher, erster und Miterfinder (falls nachstehend mehrere Namen aufgeführt sind) des Gegenstandes bin, für den dieser Antrag gestellt wird und für den ein Patent für die Erfindung mit folgendem Titel beantragt wird:

deren Beschreibung:

- ☐ ist beigefügt
- ☐ wurde angemeldet am _____

unter der US-Anmeldenummer oder unter der Internationalen Anmeldenummer im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT)

_____ und am _____
_____ abgeändert (falls zutreffend).

Ich bestätige hiermit, daß ich den Inhalt der oben angegebenen Patentanmeldung, einschließlich der Ansprüche, die eventuell durch einen oben erwähnten Zusatzantrag abgeändert wurde, durchgesehen und verstanden habe.

Ich erkenne meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Titel 37, Code of Federal Regulations, § 1.56 von Belang sind.

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

ANTIMICROBIAL COPOLYMERS

the specification of which:

- ☐ is attached hereto.
- ☒ was filed on March 30, 2000
as United States Application Number or PCT International Application Number

PCT/EP00/02799
_____ and was amended on _____
_____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

German Language Declaration

Ich beanspruche hiermit ausländische Prioritätsvorteile gemäß Title 35, US-Code, § 119(a)-(d), bzw. § 365(b) aller unten aufgeführten Auslandsanmeldungen für Patente oder Erfinderurkunden, oder § 365(a) aller PCT internationalen Anmeldungen, welche wenigstens ein Land ausser den Vereinigten Staaten von Amerika benennen, und habe nachstehend durch ankreuzen sämtliche Auslandsanmeldungen für Patente bzw. Erfinderurkunden oder PCT internationale Anmeldungen angegeben, deren Anmeldetag dem der Anmeldung, für welche Priorität beansprucht wird, vorangeht.

Prior foreign application(s)
(Frühere ausländische Anmeldungen)

<u>199 21 895.1</u>	<u>Germany</u>
(Number)	(Country)
(Nummer)	(Land)
(Number)	(Country)
(Nummer)	(Land)

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority claimed

Priorität
beansprucht

May 12, 1999
(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

☒ ☐
Yes No
Ja Nein

(Day/Month/Year Filed)
(Tag/Monat/Jahr der Anmeldung)

☐ ☐
Yes No
Ja Nein

Ich Beanspruche hiermit Prioritätsvorteile unter Title 35, US-Code, § 119(e) aller US-Hilfsanmeldungen wie unten aufgezählt.

(Application No.)
(Aktenzeichen)

(Filing Date)
(Anmeldetag)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

(Application No.)
(Aktenzeichen)

(Filing Date)
(Anmeldetag)

Ich beanspruche hiermit die mir unter Title 35, US-Code, § 120 zustehenden Vorteile aller unten aufgeführten US-Patentanmeldungen bzw. § 365(c) aller PCT internationalen Anmeldungen, welche die Vereinigten Staaten von Amerika benennen, und erkenne, insofern der Gegenstand eines jeden früheren Anspruchs dieser Patentanmeldung nicht in einer US-Patentanmeldung, bzw. PCT internationalen Anmeldung in in einer gemäß dem ersten Absatz von Title 35, US-Code, § 112 vorgeschriebenen Art und Weise offenbart wurde, meine Pflicht zur Offenbarung jeglicher Informationen an, die zur Prüfung der Patentfähigkeit in Einklang mit Title 37, Code of Federal Regulations, § 1.56 von Belang sind und die im Zeitraum zwischen dem Anmeldetag der früheren Patentanmeldung und dem nationalen oder im Rahmen des Vertrags über die Zusammenarbeit auf dem Gebiet des Patentwesens (PCT) gültigen internationalen Anmeldetags bekannt geworden sind.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application

PCT/EP00/02799

(Application No.)
(Aktenzeichen)

March 30, 2000

(Filing Date)
(Anmeldetag)

pending

(Status) (patented, pending, abandoned)
(Status) (patentiert, schwebend, aufgegeben)

(Application No.)
(Aktenzeichen)

(Filing Date)
(Anmeldetag)

(Status) (patented, pending, abandoned)
(Status) (patentiert, schwebend, aufgegeben)

Ich erkläre hiermit, daß alle in der vorliegenden Erklärung von mir gemachten Angaben nach bestem Wissen und Gewissen der Wahrheit entsprechen, und ferner daß ich diese eidesstattliche Erklärung in Kenntnis dessen ablege, daß wissentlich und vorsätzlich falsche Angaben oder dergleichen gemäß § 1001, Title 18 des US-Code strafbar sind und mit Geldstrafe und/oder Gefängnis bestraft werden können und daß derartige wissentlich und vorsätzlich falsche Angaben die Rechtswirksamkeit der vorliegenden Patentanmeldung oder eines aufgrund deren erteilten Patenten gefährden können.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

German Language Declaration

VERTRETUNGSVOLLMACHT: Als benannter Erfinder beauftrage ich hiermit den (die) nachstehend aufgeführten Patentanwalt (Patentanwälte) und/oder Vertreter mit der Verfolgung der vorliegenden Patentanmeldung sowie mit der Abwicklung aller damit verbundenen Angelegenheiten vor dem US-Patent- und Markenamt: (Name(n) und Registrationsnummer(n) auflisten)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; William E. Beaumont, Reg. No. 30,996; Jean-Paul Lavalle, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrauch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; William T. Enos, Reg. No. 33,128; Michael E. McCabe, Jr., Reg. No. 37,182; Bradley D. Lytle, Reg. No. 40,073; and Michael R. Casey, Reg. No. 40,294, with full powers of substitution and revocation.

Postanschrift: Customer No. 22850

Send Correspondence to:
OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C.
FOURTH FLOOR
1755 JEFFERSON DAVIS HIGHWAY
ARLINGTON, VIRGINIA 22202 U S A

Telefonische Auskünfte:
(Name und Telefonnummer)

Direct Telephone calls to: (name and telephone number)
(703) 413-3000

Vor- und Zuname des einzigen oder ersten Erfinders <div style="text-align: right;">1 - 00</div>	Full name of sole or first inventor Dr. <u>Peter WITERSBACH</u>
Unterschrift des Erfinders <div style="text-align: right;">Datum</div>	Inventor's signature <div style="text-align: right;">Date 09. NOV. 2001</div>
Wohnsitz	Residence <u>Windeck, Germany DEX</u>
Staatsangehörigkeit	Citizenship <u>German</u>
Postanschrift	Post Office Address <u>Zum Beuel 14, D-51570 Windeck, Germany</u>
Vor- und Zuname des zweiten Miterfinders (falls zutreffend) <div style="text-align: right;">2 - 00</div>	Full name of second joint inventor, if any Dr. <u>Beate KOSSMANN</u>
Unterschrift des zweiten Erfinders <div style="text-align: right;">Datum</div>	Second inventor's signature <div style="text-align: right;">Date 09. NOV. 2001</div>
Wohnsitz	Residence <u>Hagen, Germany DEX</u>
Staatsangehörigkeit	Citizenship <u>German</u>
Postanschrift	Post Office Address <u>Ribbertstraße 13, D-58691 Hagen, Germany</u>

(Im Falle dritter und weiterer Miterfinder sind die entsprechenden Informationen und Unterschriften hinzuzufügen.)

(Supply similar information and signature for third and subsequent joint inventors.)